ANALYSIS OF VEGETATION

DETERMINATION OF FLUORIDE - SAMPLING AND SAMPLE PREPARATION - 1400(1-69)

1. Scope

1.1 This method encompasses the sampling of vegetation and the preparation of samples for the determination of fluoride. Two procedures, considered to be completely interchangeable with respect to accuracy of results, are given for the sampling and preparation of green forage (paragraphs 6.1 and 6.2 under Procedure). A third procedure is presented for dry forage (hay and straw) (paragraph 6.3 under Procedure).

2. Summary of Method

2.1 The principle of preparation is essentially the same in each procedure. The sample is treated with calcium oxide to fix the fluoride, and the limed sample is reduced to ash at 600 C. (590°C.) Moisture is determined on a separate portion of the sample.

3. Apparatus

3.1 Kraft paper bags, new 6-10 pound capacity.

3.2 One quart wide-mouthed Bell jars with glass covers and rings or one quart polyethylene containers with tight fitting, polyethylene, snap covers.

3.3 Porcelain, Inconel[1] or nickel casseroles or dishes, approximately 135 mm in diameter and having a capacity between 750 and 1000 ml.

[1]Precision Metal Spinning Company, 9825 S. Dixie Highway, Clarkston, Michigan.

3.4 Scaltite cardboard containers, new one-quart capacity.

3.5 Wiley cutting mill equipped with a plate having 2-mm holes.

3.6 Nickel beakers, 250 ml.

3.7 Wide-mouthed Erlenmeyer flasks, 250 ml with rubber stoppers.

3.8 Garden shears or scissors with 4-5 in. blades.

3.9 Drying Oven, forced draft.

4. Reagents

4.1 Calcium oxide, specially prepared, low fluoride (obtainable from Alcoa Research Laboratories). Prepare a slurry of 15 g of CaO in one liter of distilled water.

4.2 Sodium hydroxide, pellet.

4.3 Silver perchlorate solution, 50% (50 g in 50 ml of distilled water).

5. Sampling

5.1 Representative samples will be selected. The following rules serve as a general guide for the collection of samples:

(a) Permission will be obtained from the owner to collect the sample.

(b) Samples shall be collected only from areas being actively grazed or harvested for hay. This does not mean, though, that the field must be in the process of being grazed at the time the sample is taken but that it is being used for that purpose. One composite sample will be selected from each area.

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(c) One control sample must be taken from a location completely out of the area of potential fumigation. Should the fluoride content of this sample exceed the normal background values, a check must be made starting with resampling of the control area, to ascertain whether, in fact, the sample is high in fluoride or the high value results from some source of contamination either in the sample collection procedure or in the analysis.

(d) Samples obviously contaminated with road dust, fertilizer, and dust from nearby plowing (or mining) operations will be avoided. Thus, areas near roads or fence rows are not suitable for collection of the samples. Samples shall be taken from plants having sufficient height to avoid ground splash.

(e) Samples shall not be taken during a 24-hour period following a rainfall.

(f) Do not sample row crops that will not be foraged.

(g) The samples should include all portions of the vegetation that are normally consumed by the grazing animals. Samples will generally include all vegetation above the soil splash line. Shears are used to cut the samples so that soil splash up and roots containing soil may be avoided.

(h) Record in a permanent record book a complete description of the sample including:

1. Location

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2. Type of Vegetation
3. Date of Sampling
4. Weather Conditions Prior to Sampling

6. Procedure

6.1 Green Vegetation--Grass, Leaves, etc.

6.1.1 Place alternate cuttings of the vegetation in sampling jars, for the determination of fluoride, and in weighed, 250-ml Erlenmeyer flasks for the determination of moisture. Stopper the flasks tightly and identify both jar and flask.

6.1.2 Add lime to the sample for the determination of fluoride and determine sample weight by one of the following procedures:

(a) Weigh 3g portions of calcium oxide into clean, dry sample containers. Recover and weigh closed containers with the calcium oxide, recording weights and container identities before going to the field. Reweigh the containers and their contents after samples are collected and subtract the original container weight to determine the green sample weight, or

(b) Add 200 ml of calcium oxide slurry (15 g CaO/l) to the sampling jar, seal and weigh jar before going to the field. Reweigh the jar after collecting the sample and subtract the weight of the jar and slurry to determine the green sample weight.

Lime is added to green vegetation samples to fix the fluoride. If the samples are to be analyzed within a few hours after collection,

the calcium oxide may be added immediately on return to the laboratory. Even with the addition of lime, storage of green vegetation at room temperature should be kept at an absolute minimum. Fermentation of the sample may result in the loss of fluoride.

6.1.3 After calculating the weight of the sample, transfer the contents of the sampling jar quantitatively into a procelain casserole[2] and rinse the jar with water, adding the rinsings to the sample. Cover the vegetation with water, add a few drops of phenolphthalein, and mix.

6.1.4 Moisture Determination

6.1.4.1 Weigh the 250-ml Erlenmeyer flasks containing 10 to 25 g of unlimed sample, dry 24 hours at 105 C, cool in a desiccator, and reweigh.

6.1.5 Calculation

$$\% \text{ Moisture} = \frac{\text{g of loss} \times 100}{\text{g of sample}}$$

6.1.6 Ashing and Fusion

6.1.6.1 Carry a blank, containing 200 ml of calcium oxide slurry through the entire procedure along with the samples.

6.1.6.2 Digest the prepared sample in the casserole or Inconel dish on a hot plate and add calcium oxide as required to keep the water alkaline. If additional calcium oxide is required to maintain alkalinity, the amount of the addition is recorded so that adjustment of the blank value may be calculated. Stir occasionally and evaporate

[2] Or Inconel dish.

to dryness. Ash the sample on the hot plate as completely as possible in order to prevent the dry material from bursting into flame when it is placed in the muffle. Transfer to a muffle furnace at 600 C and ignite until ashing is complete, as indicated by a white or light gray ash.

6.1.6.3 After cooling, partially pulverize the ash with a pestle and mix thoroughly. Scrape to remove any adhering material and weigh the entire contents of the casserole recording the weight to the nearest 10 mg, e.g. 7.63 g or 9.12 g. Transfer the ash to a stoppered bottle.

6.1.6.4 At this point introduce a second, or reagent blank and carry it through the remainder of the procedure along with the samples and the calcium oxide blank.

6.1.6.5 Weigh 1.00 g of ash and transfer to a nickel beaker. Add 5 g of sodium hydroxide pellets and fuse for a few minutes, over a Fisher burner. Allow to cool, wash down with water, and heat to disintegrate the melt. Proceed as indicated in Preparation for Distillation by Method 913A (paragraph 7).

6.2 Green Vegetation--Oven Dried Procedure

6.2.1 Collect vegetation samples in Kraft paper bags. Fold over the top of the bag, secure with a paper clip, and mark the sample identity on the bag with a ballpoint pen at the time of sampling.

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6.2.2 In the laboratory open the paper bag and roll down the top to expose the sample. Place in a drying oven at 80C and reduce the moisture content to approximately 5%. Sixteen hours (overnight) are usually sufficient for most samples if the oven is not overcrowded and is well ventilated.

6.2.3 Reduce the entire dried sample in the Wiley mill and mix thoroughly. Place the ground sample in an adequately identified Sealtite container. This ground material is the laboratory sample and may be retained indefinitely without change.

6.2.4 Accurately weigh approximately 5 g of sample into a 250-ml nickel beaker, the sample size being dependent on the expected fluoride content. Accurately weigh a second 1 to 2 g portion of the sample into a 50-ml beaker for a moisture determination. Determine the moisture by drying at 105 C.

6.2.5 Carry a blank containing 20 ml of CaO slurry through the entire procedure along with the samples. To the sample in the nickel beaker, add 20 ml of the CaO slurry and, if necessary, sufficient water to thoroughly wet the sample. Mix carefully and test the suspension with phenolphthalein. The suspension must be alkaline. Digest the prepared sample on a hot plate to char organic material and prevent loss through flaming when furnace ignition is commenced. Transfer the sample to a muffle furnace at 600 C and ignite until ashing is complete as indicated by a white or light gray ash (about 2 hours).

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6.2.6 At this point introduce a second, or reagent blank and carry it through the remainder of the procedure along with the samples and calcium oxide blank.

6.2.7 Add 5 g of sodium hydroxide pellets and fuse over a gas burner. Cool, rinse down the walls of the beaker with water and warm to dissolve the fusion. Proceed as indicated in Preparation for Distillation by Method 913A (paragraph 7).

6.3 Dry Forage (Hay and Straw)

6.3.1 Stacks of hay or straw must be laid apart to provide exposure for representative sampling. Bales of hay must be opened to permit representative sampling. Sheared portions will be collected in Kraft paper bags and treated as indicated in paragraph 6.2, Green Vegetation--Oven Dried Procedure, except that the drying time may be shortened to 4 hours.

7. Preparation for Distillation by Method 913A

7.1 Transfer the contents of the nickel beaker to a modified Claissen flask containing 5 to 6 soft glass (not Pyrex) glass beads. In addition to the blank containing calcium oxide, carry a reagent blank. Insert in the neck of the flask a rubber stopper through which pass a thermometer and a glass inlet tube. Set the flask in the 2-in. diameter hole in the metal plate and connect to a condenser. Rinse the sides of the beaker with 50 ml 5+70 <75ML. of perchloric acid (70 to 72%) OR and add 1 ml of silver perchlorate solution. Transfer to the distilling flask by means of a small

funnel attached to the glass inlet tube. Rinse the beaker and add the rinsings to the flask. Mix the contents of the flask and proceed as indicated in Method 913A.

7.2 Titration of the distillate for fluoride estimation will be by the procedure presented in Method 914D.